

(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 205 243 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
15.05.2002 Bulletin 2002/20

(51) Int Cl.7: **B01J 35/00**, B01J 21/06,
B01J 37/02

(21) Application number: 00203953.5

(22) Date of filing: 09.11.2000

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

- **Minero, Claudio**, Univ. degli Studi di Torino
10125 Torino (IT)
- **Pelizzetti, Ezio**, Univ. degli Studi di Torino
10125 Torino (IT)

(71) Applicant: **Neomat S.A.**
1219 Luxembourg (LU)

(74) Representative: **Luppi, Luigi et al**
Luppi & Crugnola S.r.l.
Viale Corassori, 54
41100 Modena (IT)

(72) Inventors:
• **Maurino, Valter**, Univ. degli Studi di Torino
10125 Torino (IT)

(54) **Preparation of firmly-anchored photocatalytically-active titanium dioxide coating films with non-gelled organic-doped precursors**

(57) The production of thin films of titanium dioxide in the anatase crystallographic structure performing with high photocatalytic activity is made possible on transparent inorganic substrates. The film is produced through deposition (roll, spray, dip coating) of a stable liquid precursor containing an inorganic or metal-organic compound of titanium(IV) partially or totally hydrolyzed in the presence of acid, surfactants and, eventually, s-triazine derivatives. The last improve the photocatalytic activity of the film and its resistance to bases. The gelation of the precursor is blocked by the presence

of acid and/or a suitable surfactant. The absence of gelification avoids the need of further reprecipitation of the gel, as usually required in the common sol-gel methods. The liquid precursor is stable in air, and storable for some months without alteration. Thin films produced in this way show optimal transparency in the visible and induce strong abatement of pollutants under illumination, either in the aqueous or gas phase. Applications range from water purification, waste abatement, air cleaning and deodorization, indoor disinfecting, and self-cleaning transparent glass, goods, fabric, and other architectural or functional elements.

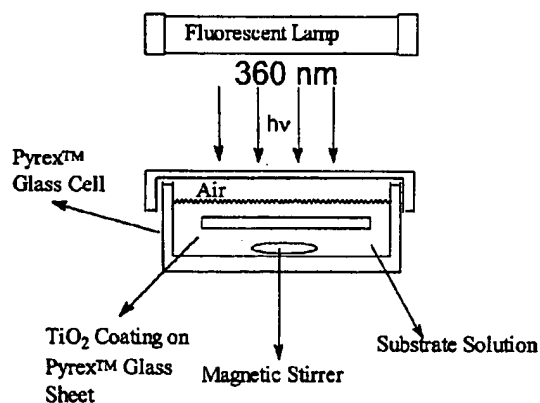


Figure 2.

EP 1 205 243 A1

Description

5 **[0001]** The invention concerns a process for the coating of inorganic transparent supports with a functional material consisting of thin films containing TiO_2 according to the preamble of claim 1. Such films, under light irradiation, can catalyze several redox processes. These processes result in several applications like pollutant abatements in gaseous and water streams, water potabilization, deodorizing and antibacterial functions for indoor air conditionings, self cleaning architectural ornaments and elements.

10 **[0002]** In the published technical and scientific literature the principle of semiconductor photocatalysis and the possible application fields are deeply described, in particular for the organic pollutant abatement from air and aqueous systems (E. Pelizzetti, N. Serpone, E. Pramauro, M. Barbeni, E. Borgarello, M. Graetzel, *Nouv. J. Chim.* 1984, 8, 547-550; E. Pelizzetti, N. Serpone, *Heterogeneous Photocatalysis*, J. Wiley and Sons 1989; E. Pelizzetti, C. Minero, V. Maurino, *Adv. Colloid and Interf. Sci.* 1990, 32, 271-316; D. F. Ollis, H. Al-Ekabi, *Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam, 1993). Practical examples of photocatalytic applications include the organic material mineralization in industrial waste, water potabilization, the recovery of noble metals from water, air cleaning in general, and in particular in indoor thermal and environmental air conditioning, deodorization, the manufacturing of architectural ornaments and elements (glass and shop windows, windows) that requires less duty for cleaning, the fabrication of lamps and shielding of them, accumulating less dirt. In addition the photocatalytic materials have disinfecting properties, which make them useful for keeping germ free the medical rooms.

20 **[0003]** The primary events, on which photocatalytic treatment is based on, have been matter of ample research as witnessed by the huge literature published in the field (see for example the review in E. Pelizzetti, C. Minero, *Mechanism of the photooxidative degradation of organic pollutants over titanium dioxide particles*, *Electrochim. Acta*, 38, 47-55 (1993) in order to have a view on the state of art). They imply the absorption by the semiconductor of a photon having energy greater than the band gap. As far as titanium dioxide is concerned, photons must have wavelength below 380-400 nm. These photons are still present in the solar spectrum at the sea level. Following absorption an electron/ hole pair is formed. Then the electronic carriers can recombine, or migrate to the surface where, either by direct electron transfer or by trapping on surface sites and their subsequent reaction, react with the solvent (e.g. water if it is present) or organic and inorganic species adsorbed or transported to the interface. Some of these species are oxidized and some reduced, as oxygen and other electron scavengers do. In the presence of oxygen numerous organic substances are oxidized until full mineralization is achieved, so that carbon dioxide and inorganic ions are formed. The main advantage of the photocatalytic process lies in his ability to mineralize organic compounds, overcoming the deficiencies of other cleaning technologies that simply transfer the pollutants from one phase to another one. The role of the consecutive and parallel kinetic processes on the overall performance of the process has been subject of several theoretical and experimental studies (see for example C. Minero, *Kinetic analysis of photoinduced reactions at the water semiconductor interface*, *Catalysis Today*, 54, 205-216 (1999) and the literature cited therein).

35 **[0004]** The main issues on the practical application of the photocatalytic processes concern: a) the activity of the catalyst (or its photon efficiency), that is alleged insufficient for available semiconductor materials. b) the availability of a low cost semiconductor firmly anchored on a transparent support. c) the stability of the photocatalytic coating to exposure to alkaline media and surfactants. d) the homogeneity of the films and their transparency, that are an important issue for applications where efficient transmission of visible light, uniform features and aesthetic prerequisites are needed. Deposition methods such as sputtering and chemical vapor deposition are costly and not suitable for support on any shape. The deposition on the materials concerned in the present invention of previously prepared powders of titanium dioxide (see for example the EP patent publications Nos. 792687A1, 684075A1, 866101A1) usually leads to coated materials that are not resistant to abrasion, with insufficient optical quality, either for homogeneity or transparency, or it requires the use of adhesives, either inorganic melting agents or polymers, often having adverse effects on the catalyst activity, its performance in the photocatalytic process, and limiting its efficacy toward its final scope. Finally, the partially opaque surfaces obtained in this way scatter more light, compromising the usefulness in applications where good transparency is required.

45 **[0005]** The previous issues could be improved using coating procedures with liquid precursors (by spray, roll or dip-coating) prepared by preventing, after the solvolysis, the gelation of sols of Ti(IV) . This approach is inexpensive, allows a great freedom of formulation (composition of the liquid precursor as amount and type of solvents, dopants, starting materials containing Ti(IV)), is applicable to supports in a variety of shapes and sizes, and does not require the time-consuming re-peptization of the gel or the preformed oxide particles as usual sol-gel procedures.

50 **[0006]** The European patent publication No. 737513A1 claims the generic use for photocatalytic purposes of thin and transparent (to visible spectrum) films of TiO_2 deposited on transparent substrates, with or without an in-between layer, by using solutions of Ti(IV) alkoxides and chlorides. However, such possibility has been demonstrated in the scientific literature well before the patent. The scientific literature reports on the making of thin films of titanium dioxide on transparent supports (in particular glass beads) and their application to both oxidative (organic pollutant destruction in aqueous systems) and reductive processes (noble metal recovery from water, Cr(VI) decontamination). See for

example: E. Borgarello, N. Serpone, M. Barbeni, C. Minero, E. Pelizzetti, E. Pramauro "Putting Photocatalysis to Work", in "Homogeneous and Heterogeneous Photocatalysis", E. Pelizzetti and N. Serpone Eds, Reidel, Dordrecht, 1986, pages 673-689; N. Serpone, E. Borgarello, R. Harris, P. Cahill and E. Pelizzetti, Sol. En. Mat., 1986, 14, 121; J. Sabate, M.A. Anderson, M.A. Aguado, J. Gimenez, S. Cervea-March, C.G. Hill, Journal of Molecular Catalysis, 1992, 71, 57-68; M.A. Anderson, M.S. Gieselmann, Q.Xu, Journal of Membrane Science, 1988, 39, 243-258. In addition, the European patent 737513A1 does not disclose the procedure and the formulation details for the production of the precursors used in the coating, neither in the claims nor in the examples. In the examples one composition of the liquid precursor utilizes acetylacetone as solvent, which is not included in the present invention.

[0007] The generic preparations that can be imagined from the technical scientific and patented literature are not usually stable with time, may gel and settling down solid particles becoming useless for industrial preparations, or producing coating films of insufficient optical and aesthetic quality either for transparency or homogeneity. The resistance of these films to abrasion and chemical agents is often unknown. Some modifications supposed to increase the photocatalytic activity of the film are often indicated, like addition of traces of metals, without the detailed indication of the effects of any of these. It is a long time since the scientific literature reported the effects of microscopic metal islands on several crystalline modification of titanium dioxide (see for example M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, Environmental application of semiconductor photocatalysis, Chem. Rev. 95, 69-96 (1995); D. F. Ollis, H. Al-Ekabi, Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993), and its doping with metal ions. Not always the photocatalytic activity is improved. Here the first case of organic doping with beneficial influence on the photocatalytic activity is reported.

[0008] The process of the present invention is defined in the characterizing portion of claim 1.

[0009] The present invention pertains to a process to coat transparent inorganic supports (for example alkaline and borosilicate glass, quartz, fused silica) with thin films of titanium dioxide in the anatase crystalline form having relevant photocatalytic activity, and the use of organic dopants to improve the photocatalytic activity. The coatings realized with the present methodology show 0.05 to 10 μm film thickness, are resistant to atmospheric factors and abrasion, are thoroughly and absolutely homogeneous, and transmissive on average over 80% in the visible spectrum. The process consists of the deposition on the support of a stable liquid precursor made of inorganic or metal-organic compounds of Ti(IV) partially or totally hydrolyzed, and surfactants, and/or acids, and a suitable organic doping, in particular s-triazine derivatives, included to improve the photocatalytic activity and mechanical resistance, followed by a thermal treatment to achieve the film densification. The claimed procedure allows avoiding the gelification of the precursor, running away the need of further re-peptization of the gel as usually required in the common sol-gel methods. The liquid precursor is stable in air, and storable for some months without alteration. The films realized through the reported procedure do not decrease significantly either their photocatalytic activity or the adhesion to the support after treatment with alkaline solutions embodying also surfactants. The doping with s-triazine derivatives results in an average improvement of the photocatalytic activity of 2-3 times with respect to non-doped films.

[0010] The present invention concerns the manufacture of homogeneous and transparent (in the visible spectrum) coating films of titanium dioxide in the anatase crystalline form on inorganic transparent supports, like different types of glasses, quartz, fused silica, through the deposition by dip-coating, spray or roll of liquid precursors of which the composition is disclosed. The invention improves on the issues previously discussed, and leads to photocatalytic activities superior to those obtained in the absence of nitrogen-containing dopants that are included in the formulation below disclosed. The process requires no interlayer or binder between the support and the photocatalytic film.

[0011] The liquid precursor is prepared by hydrolysis or partial or total solvolysis of compounds of tetravalent titanium under conditions in which the gelation is avoided. The concentrations of Ti(IV) range from 0.1% to 35% by weight. Titanium compounds included in the formulation are alkoxides, and in particular tetrabutoxy-ortho-titanate, tetrapropoxy-ortho-titanate, tetraisopropoxy-ortho-titanate, or halides, in particular the tetrachloride, or other kind of complexes like bis(ammonium lactate)dihydroxyde titanium(IV). The solvolysis is carried out from 1 min to 36 hours, at temperatures ranging from 5°C to the solvent boiling point, eventually under pressure (1-20 atm) at temperatures ranging from 0°C to 120 °C. The solvolysis is necessary to form compounds of Ti(IV) that are less volatile than the original compounds, unable to vaporize during the subsequent thermal treatment, and showing good film sticking properties, and sufficient thickness to the support. Otherwise, the precursor could be partially or completely vaporized and lost during the thermal treatment, with formation of irregular and/or discontinuous or no coatings. The water concentration needed by the hydrolysis ranges from 0.1% to 30% by weight.

[0012] The solvents needed in the formulation of the liquid precursors are alcohols, also polyfunctional and containing oxygen in ether bonds, carrying 1-10 carbon atoms and 1-6 oxygen atoms, or lactones containing 4-6 carbon atoms, or their mixtures in all proportions. The solvent choice is based on the procedure used for the deposition (dip-coating, spray, roll-coating) and the desired depth of the resulting coating film of titanium dioxide.

[0013] The gelation of the liquid precursor, either contemporary to the preparation step or when the precursor is stored before deposition renders it incompatible with the deposition with dip-coating, spray or roll-coating, especially if thin films below 10 μm are desired. To avoid gelation an inorganic or organic acid is added at concentrations ranging

from 0.1% to 20% by weight and/or a surfactant of type nonionic, or cationic, or anionic, or zwitterionic and their mixtures in all proportions, at concentrations ranging from 0.01% to 50% by weight. The presence of surfactant and/or the acid as the additional effect of inhibiting the formation in the liquid precursor of titanium dioxide particles having diameter larger than 100 nm, that will form coating films less resistant to the abrasion and less uniform. The disclosed formulation leads to the formation of polymeric titanates that under the thermal treatments hereafter disclosed form compact and non porous anatase films showing excellent adhesive properties on the supports above specified. The gelation processes and formation of particulate titanium dioxide are inhibited by the presence of the acid and/or the surfactant at temperatures ranging from -10°C to 100 °C. At ambient temperature the disclosed formulation renders the precursor stable against gelation and particle formation and settling for 6 to 12 months, depending on the composition.

[0014] Among inorganic acids the following are suitable: nitric acid, sulfuric acid, phosphoric acid, hydrofluoric acid, hydrochloric acid, perchloric acid and their mixtures in all proportions. Among organic acids are adequate those with linear or branched chains, also with 2 or 3 carboxylic groups and/or containing hydroxyl-, and/or chloro-, and/or fluoro-, and/or bromo- groups, or benzoic acid and its derivatives, and/or other carboxylic acid with aromatic structure.

[0015] Non-ionic surfactants alkyl- or alkylarylethoxylate and their mixtures in all proportions (for example the commercial products Brij 30, Brij 35, Triton X100), and/or alkyl or alkylethoxysulphate anionic surfactants (for example sodium dodecyl sulphate), and/or alkylbenzene sulphonate, and/or cationic surfactants, e.g. cetyltrimethylammonium bromide, and/or zwitterionic surfactants, like betaine derivatives, are among the surfactants useful to block the gelation and TiO₂ particle growth.

[0016] The s-triazine ring, which is characteristic of compounds like melamine, cyanuric acid, cyanurates, cyanuric chloride, was found to have a positive influence on the photocatalytic activity when added as dopant to the precursor formulation. Many s-triazine compounds show excellent thermal stability (melamine placed in a sealed vial is stable to red heat, see for example E. M. Smolin, L. Rapoport, s-Triazines, in: A. Weissenberg Ed., The Chemistry of Heterocyclic Compounds, Vol. 13A, Wiley Interscience, New York, 1959). The s-triazine derivative doping gives the photocatalytic film a good stability against treatment with alkaline media and surfactants, concerning both adhesion on the support and the photocatalytic activity. The photoactivity of the doped film is increased by a factor 1.5-3 when in the precursor formulation is introduced a selected s-triazine derivative in concentration ranging from 0.1 to 20% by weight.

[0017] The coating with the precursor made by the above cited procedures, is followed by a thermal treatment lasting 10-200 min at temperatures ranging from 300°C to 800°C, in the presence of a gas phase containing oxygen in the range 1% to 50% by volume, in order to fully convert the precursor in microcrystalline anatase TiO₂, and obtain a coating with good mechanical and chemical stability.

[0018] The formulations and procedures here disclosed allow the manufacture of homogeneous and transparent (in the visible spectrum) coating films of titanium dioxide in the anatase crystalline form on inorganic transparent supports. The coating films show relevant photocatalytic activity. The formulations disclosed allow the preparation of liquid, non-gelled and stable precursors for film fabrication with low cost coating procedures (dip, spray or roll coating). The absence of gelification avoids the need of further re-peptization of the gel, as usually required in the common. sol-gel methods. The liquid precursor is stable in air, and storable for some months without alteration. The supported films obtained show very good mechanical properties, adhesiveness to the support and scratching resistance without the intervention of an in-between layer.

[0019] This is the first report of an advantageous organic doping of titanium dioxide films. Nitrogen containing organic dopants, like s-triazine compounds, enhance significantly the photocatalytic activity of the film. Moreover, the organic doped films do not decrease significantly either their photocatalytic activity or the adhesion to the support when treated with alkaline solutions embodying also surfactants.

[0020] Table 1 shows the best mode of carrying out the invention by one example of the precursor composition used for the coating of the films thereof, in agreement with the claim 8 in the absence of the s-triazine derivative doping, of the type of support used and the temperature of the thermal treatment. Sometimes the preparation has to be carried out under nitrogen atmosphere, depending on the organic solvent. A thermal aging could improve the precursor performance by completing the hydrolysis and/or solvolysis of the original titanium compound. After thermal aging, the exemplified formulation does not gel nor nucleate solid particles within 6-12 months if stored in the dark and in a closed container at ambient temperature ($\leq 25^{\circ}\text{C}$).

Table 1.

5	Example of film coating on inorganic transparent support according to the disclosed procedure, showing the weight % of Ti(IV) starting compound, acid, surfactant and solvent, the coating procedure and details of the thermal treatment.		
	Step 1: Liquid precursor formulation		
	<i>Component</i>	<i>Weight %</i>	<i>Preferred Weight %</i>
10	Isopropyl alcohol	46 to 88.7	76
	Phosphoric acid 85%	0.1 to 10	0.8
	Water	0.2 to 4	2.9
	Brij 30	1 to 20	2.3
15	Tetrapropoxy-ortho-titanate	10 to 20	18
	Step 2: Aging : closed container for 24 h at 60°C		
	Step 3: Coating and film densification		
20	Deposition procedure	Dip-coating, rate 12 cm min ⁻¹	
	Support	Pyrex glass.	
	Thermal treatment	400 °C for 30 min under forced air flow.	

25 **[0021]** Figure 1 reports the results of the tests on photocatalytic activity showed by a TiO₂ film prepared according to claim 8 (without s-triazine derivative doping). The activity was checked by measuring the degradation rate of a model organic compound in aqueous solution (see the legend of Figure 1 for details). Figure 2 shows a scheme of the experimental setup employed for the photoactivity tests in the liquid media. After 15 hours of irradiation the dissolved organic carbon (DOC) was no longer detectable with standard catalytic combustion DOC measurement apparatus (Shimadzu TOC 5000). The film activity does not show any appreciable variation even after 50 tests. The irradiation of a control (Pyrex glass sheet without TiO₂ film) did not lead to any appreciable decrease of the organic substrate concentration, and consequently of DOC, within 24 hours, thus confirming that phenol degradation is due to the photocatalytic activity of the TiO₂ coating.

35 **[0022]** The film adhesion on the support, and the abrasion resistance are not adversely affected by a treatment with hot concentrated sulfuric acid and aqueous sodium carbonate (10% by weight in water). The film is not scratched by a pen eraser, and it is not removed by a series of 20 abrasions with fine grit paper (1000 mesh) under a 3 kg cm⁻² load. These coating properties are crucial in the above cited applications of photocatalytic films (e.g. purification and/or detoxification of water and wastewater), where abrasion from liquids and/or solid suspended matter can remove a loose coating, or for application where washings with commercial detergents (acid or alkaline surfactant solutions) can not be excluded.

40 **[0023]** Figure 3 shows test results on the photocatalytic activity in gaseous phase. The film activity was measured through the disappearance rate of gaseous toluene (5-100 ppbv) in a gas-solid photoreactor. See figure 4 for a scheme of the test apparatus. The degradation rate of toluene follows a pseudo-first order kinetic law for concentration up to 100 ppbv with a decay constant not dependent from the substrate concentration. Thus the degradation rate increases linearly with the increase of the substrate concentration in the concentration range explored. Control experiments carried out irradiating the Pyrex glass support without catalyst film, showed no appreciable decrease of substrate concentration even after 70 hours of irradiation.

45 **[0024]** No persistent volatile organic compounds were formed from the degradation of toluene. These results show the suitability of the invention for applications like deodorization of indoor ambient and the purification of gaseous streams contaminated by volatile organic compounds. The use of photocatalytic films for the purification of indoor air allows the use of recirculated air as a partial substitute of fresh air, helping in cutting back heating costs in heat, ventilation and conditioning systems.

50 **[0025]** Figure 5 reports the Raman spectrum of the TiO₂ coating. It is worth to note the exclusive presence of the Raman lines of the anatase crystalline form (136, 389, 509, 631 cm⁻¹), whereas emissions from rutile are absent (440 and 620 cm⁻¹). The reported spectrum exactly matches the spectrum of microcrystalline anatase specimen. The line width indicates a microcrystalline habit of the film, excluding the presence of a large portion of amorphous zones. The spectrum was collected with a dispersive confocal Raman microspectrometer (see Figure 5 caption for details).

55 **[0026]** The photoactivity of the doped film is increased by a factor 1.5-3 when in the precursor formulation is intro-

duced a selected s-triazine derivative in concentration ranging from 0.1 to 20% by weight. The s-triazine derivative doping gives also the photocatalytic film a good stability against treatment with alkaline media and surfactants, both for the adhesion on the support, and the photocatalytic activity. Table 2 reports the preparation procedure of a TiO_2 coating doped with cyanuric chloride, according to claim 8.

Table 2.

Example of film coating doped with cyanuric chloride on inorganic transparent support according to the disclosed procedure, showing the weight % of Ti(IV) starting compound, acid, surfactant and solvent, the coating procedure and details of the thermal treatment.		
Step 1: Liquid precursor formulation		
<i>Component</i>	<i>Weight %</i>	<i>Preferred Weight %</i>
Isopropyl alcohol	36 to 87.7	71.6
Phosphoric acid 85%	0.1 to 10	0.3
Water	0.2 to 4	2.8
Brij 30	1 to 20	2.2
Tetrapropoxy-ortho-titanate	10 to 20	17.3
Cyanuric Chloride	1 to 10	6.0
Step 2: Aging : closed container for 24 h at 60°C		
Step 3: Coating and film densification		
Deposition procedure	Dip-coating, rate 12 cm min ⁻¹	
Support	Pyrex glass	
Thermal treatment	700 °C for 30 min under forced air flow.	

[0027] Figure 6 compares the photoactivity tests of doped and undoped films prepared according to claim 8 (undoped film is prepared from a precursor without cyanuric chloride). The pseudo-first order kinetic constants for phenol disappearance are 0.14 and 0.35 hours⁻¹ for the undoped and doped film, respectively. As a result of the doping, the photocatalytic activity is increased by a factor of 2.5 under the reported experimental conditions.

[0028] The s-triazine derivative doping endows the photocatalytic film with good stability against treatment with alkaline media and surfactants, concerning both adhesion on the support, and the photocatalytic activity. Figure 7 shows the test results on the photocatalytic activity of doped TiO_2 films, prepared according to claim 8, before and after one and two treatments (24 hours immersion at a temperature of 25±5 °C) with a solution containing Na_2CO_3 (100 g L⁻¹) and sodium dodecyl sulfate (50 g L⁻¹). After the first basic treatment the decrease in the photocatalytic activity was under 10% of the initial one. The second treatment did not lead to a further decrease in the photocatalytic activity. These results confirm the good stability of the doped films against treatments with alkaline and/or surfactant solutions.

[0029] The adhesion on substrate and the resistance to abrasion of the doped films are not adversely affected also by treatment with concentrated sulfuric acid or with Na_2CO_3 10%.

[0030] The present invention is susceptible to modifications in the methods and materials, as well as alterations in the fabrication methods and equipment. Such modifications will become apparent to those skilled in the art from a consideration of this disclosure or practice of the invention disclosed herein. Consequently, it is not intended that this invention be limited to the specific embodiments disclosed herein, but that it covers all modifications and alternatives coming within the true scope and spirit of the invention as embodied in the attached claims.

[0031] In order that the application will be fully understood reference is made on the accompanying drawings:

Figure 1. Results of the tests on the photocatalytic activity of a TiO_2 film coated on Pyrex glass with a liquid substrate. The film was prepared with a non-gelled precursor having a composition according to claim 8, but without s-triazine derivative dopant. Substrate: aqueous phenol solution (1.0×10^{-4} M). (♦) TiO_2 film with an active surface of 16 cm², irradiated with a fluorescent lamp (TL K 05 40 W Philips, radiation intensity incident on the film 30 Wm⁻². See figure 2 for a scheme of the experimental set-up). (■) Control specimen (Pyrex sheet without TiO_2 film).

Figure 2. Experimental setup employed for the tests on photocatalytic activity with liquid substrates. The volume of the liquid in the cell is 35 cm³. For other data see Figure 1 caption.

Figure 3. Test results on the photocatalytic activity of a TiO_2 film coated on Pyrex glass with a gaseous substrate. The film was prepared with a non-gelled precursor having a composition according to claim 8, but without s-triazine derivative dopant. Substrate: toluene in air (20% O_2 , 1.94% H_2O , 70 L) at the concentration reported. The active surface of the TiO_2 film was 360 cm^2 , irradiation was carried out with a medium pressure Hg lamp (Philips mod. HPR 125 W HG, radiation intensity incident on the film 25 Wm^{-2}). See figure 4 for a scheme of the experimental setup. Tests on the control specimen (Pyrex glass sheet without photocatalyst) showed concentration decreases of toluene concentration under 5% after 70 hours irradiation.

Figure 4. Experimental setup employed for the evaluation of the photocatalytic activity of TiO_2 films in the degradation of volatile organic compounds and permanent gases in the gaseous phase. The gas/solid photoreactor has a volume of 70 liter, is connected to an analytical apparatus (gas-chromatograph with a quadrupolar mass selective detector, equipped with a preconcentration system, allowing detection limit of the order of few pptv for most volatile organic compounds), and to a dynamic diluter for gaseous mixture preparation.

Figure 5. Raman spectrum of a TiO_2 film coated on Pyrex glass and manufactured starting from a non-gelled liquid precursor having a composition in accordance with claim 8, but without s-triazine derivative doping. The spectrum was recorded with a Renishaw confocal microspectrophotometer mod. Raman 2000. The Raman signal intensity is reported in relative units.

Figure 6. Comparison of the photocatalytic activity of TiO_2 films undoped (♦) and doped with a s-triazine compound (■) (cyanuric chloride). Substrate: aqueous phenol solution (1.0×10^{-4} M). Other conditions as in figure 1.

Figure 7. s-Triazine derivative doped TiO_2 film stability against alkaline treatments. Substrate: aqueous phenol solution (1.0×10^{-4} M). Other conditions as in figure 1. TiO_2 film before (■) and after 24 (♦) and 48 hours (●) of treatment with a solution containing Na_2CO_3 100 g L^{-1} and sodium dodecyl sulfate 50 g L^{-1} .

Claims

1. A process for the coating of inorganic transparent supports with thin films containing TiO_2 , characterized in applying films comprising a concentration ranging from 50 to 99.9% by weight as titanium dioxide, having remarkable photocatalytic activity and thickness ranging from 0.05 to 10 μm , consisting by
 - a) dip coating, roll coating or spray coating non-gelled precursors obtained through solvolysis of Ti(VI) compounds from 1 min to 36 hours, at temperatures ranging from 5°C to the solvent boiling point, eventually under pressure (1-20 atm) at temperatures ranging from 0°C to 120 °C, eventually doped with a selected s-triazine derivative, and/or urea, and/or dicyandiamide;
 - b) thermal treating in the presence of 1% to 50% by volume of O_2 at temperatures ranging from 300 to 800 °C.
2. The process according to claim 1, characterized in that the non-gelled liquid precursors contain in their formulation the following five components:
 - a) Ti(IV) compound in concentrations ranging from 0.1% to 35% by weight, including alkoxides, and in particular tetrabutoxy-ortho-titanate, tetrapropoxy-ortho-titanate, tetraisopropoxy-ortho-titanate, or halides, in particular the tetrachloride, or other kind of complexes like bis(ammonium lactate)dihydroxyde titanium(IV) ;
 - b) water ranging from 0.1% to 30% by weight;
 - c) an organic solvent, which can be alcohols, also polyfunctional and containing oxygen in ether bonds, carrying 1-10 carbon atoms and 1-6 oxygen atoms, or lactones containing 4-6 carbon atoms, or mixtures thereof in all proportions;
 - d) an organic or mineral acid and mixtures thereof at concentrations in the range 0.1% to 20% by weight, in order to stop the precursor gelation at temperatures in the range -10 to 100 °C.
 - e) a surfactant or a surfactant mixture at a total concentration in the range 0.01% to 50% by weight, comprising non-ionic surfactants like alkyl or alkylarylethoxylate and their mixtures in all proportions, and/or alkyl or alkylethoxysulphate anionic surfactants, and/or alkylbenzene sulphonate, and/or cationic surfactants, and/or zwitterionic surfactants, like betaine derivatives.
3. The process according to claim 2, characterized in that the formulation of the non-gelled liquid precursor comprises a s-triazine derivative, and/or urea and derivatives, and/or dicyandiamide and derivatives, or mixtures thereof

in all proportions, at concentrations in the range 0.1% to 20% by weight, in order to enhance the photocatalytic activity of the TiO_2 film and its resistance to alkaline agents and surfactants, preferably cyanuric chloride in concentrations ranging from 1 to 10% by weight.

- 5 4. The process according to claims 2 and 3, **characterized in that** the solvolysis of the Ti(IV) compound contained in the precursor is carried out with water or glycols in concentrations ranging from 0.1% to 10%, preferably water and/or ethylene glycol and their mixtures in all proportions from 0.2 to 4% by weight.
- 10 5. The process according to claims 2 to 4, **characterized in that** the formulation of the non-gelled liquid precursor comprises mineral acids, like nitric or hydrochloric or perchloric or sulfuric or phosphoric or hydrofluoric acid, or mixture thereof in all proportions, at concentrations in the range 0.1% to 10% by weight.
- 15 6. The process according to claims 2 to 4, **characterized in that** the formulation of the non-gelled liquid precursor comprises an organic acid with linear or branched carbon chain, also containing more than one carboxylic functionality and/or OH groups, fluorine, chlorine, bromine, or benzoic acid and/or its derivatives, or mixtures thereof in all proportions, preferably acetic acid, at concentrations ranging from 0.1% to 10% by weight.
- 20 7. The process according to any claims 2 to 6, **characterized in that** the formulation of the non-gelled liquid precursor preferably comprises alkyl and/or alkylphenyl polyethoxylates at concentrations ranging from 1% to 20% by weight.
8. The process according to any claims 2 to 7, **characterized in that** the formulation of the non-gelled liquid precursor comprises titanium(IV) alkoxides at concentrations in the range 1% to 35% by weight, preferably 10% to 20%.

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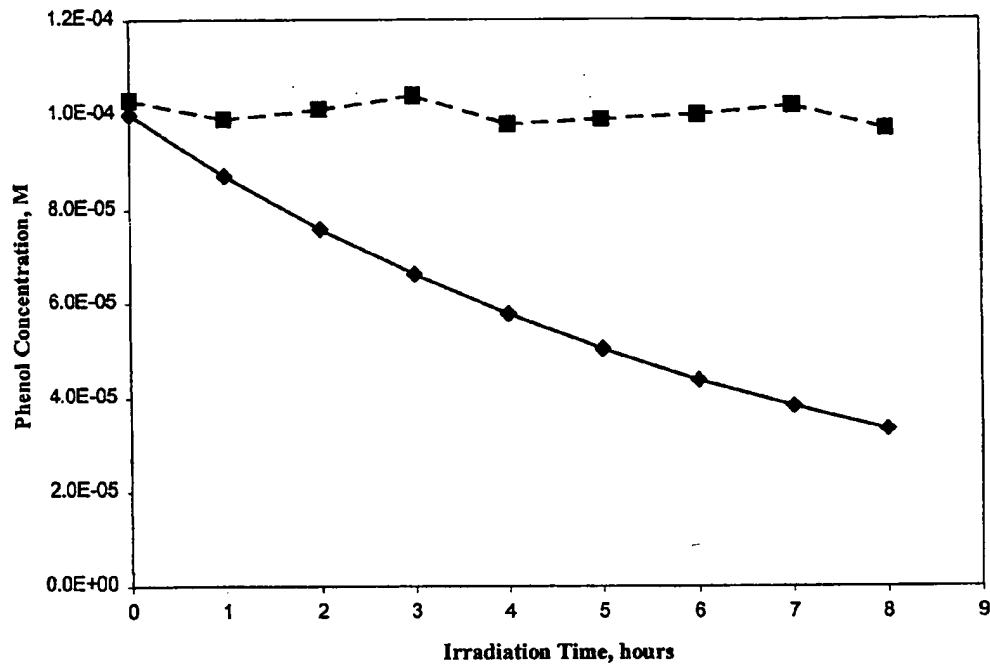


Figure 1

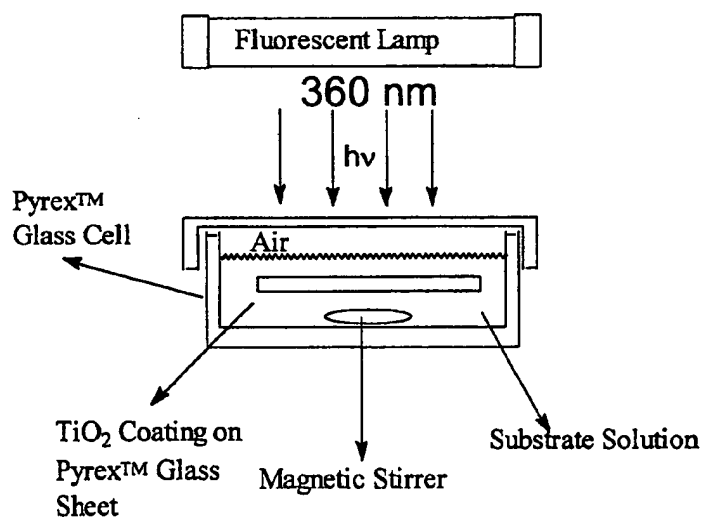


Figure 2.

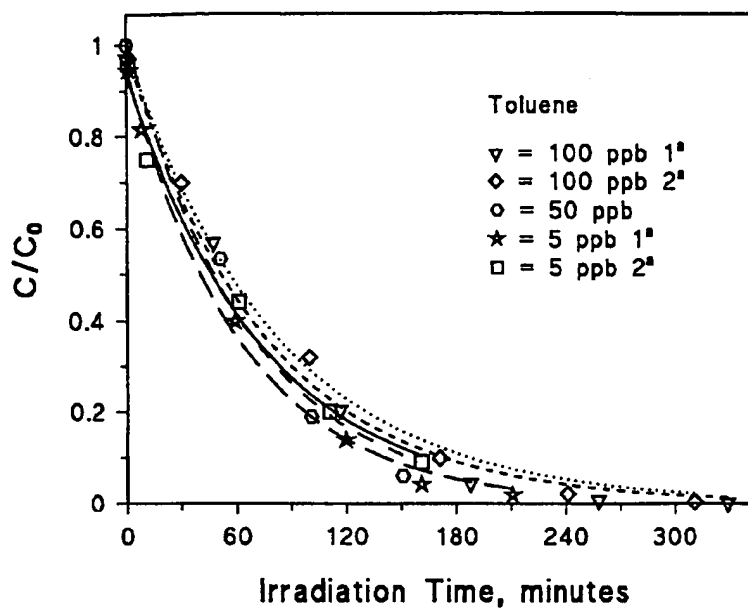


Figure 3

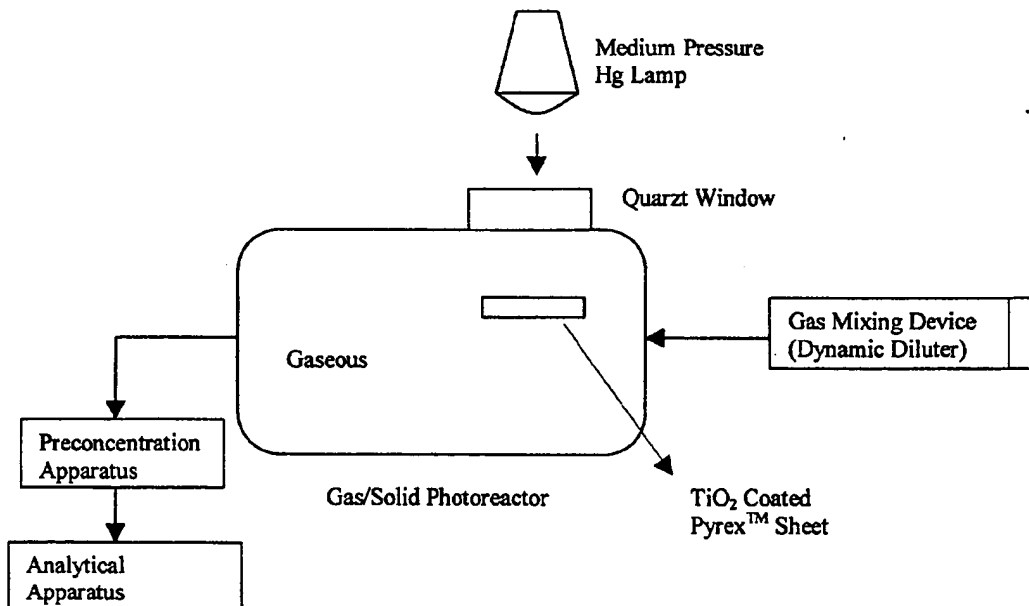


Figure 4

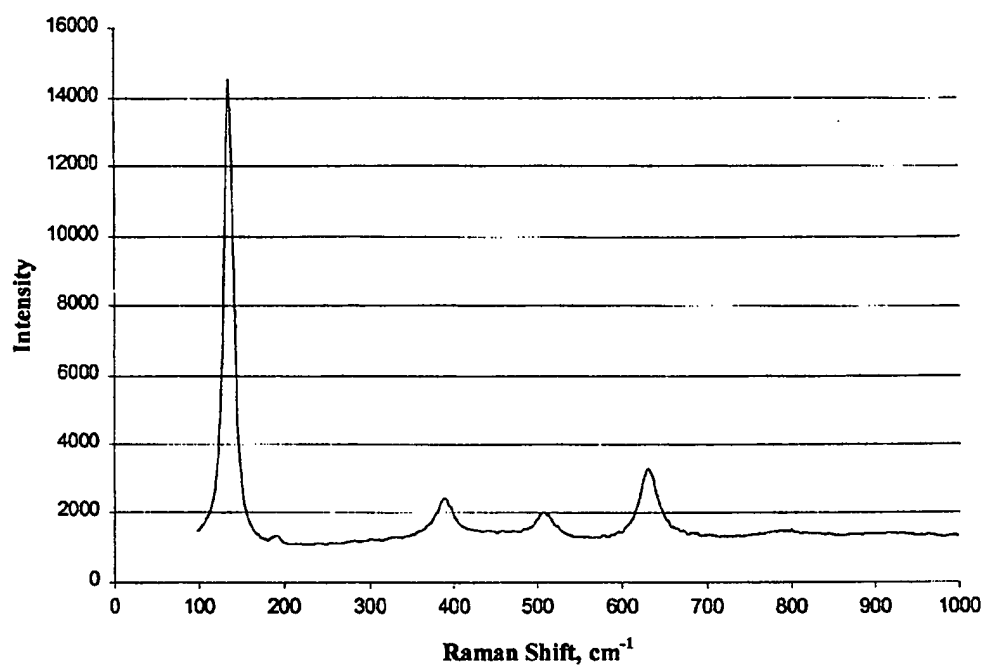


Figure 5

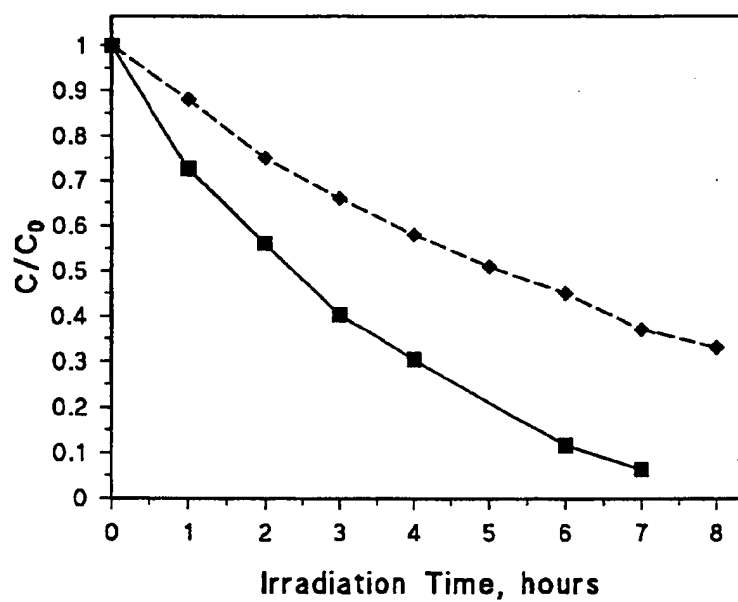


Figure 6

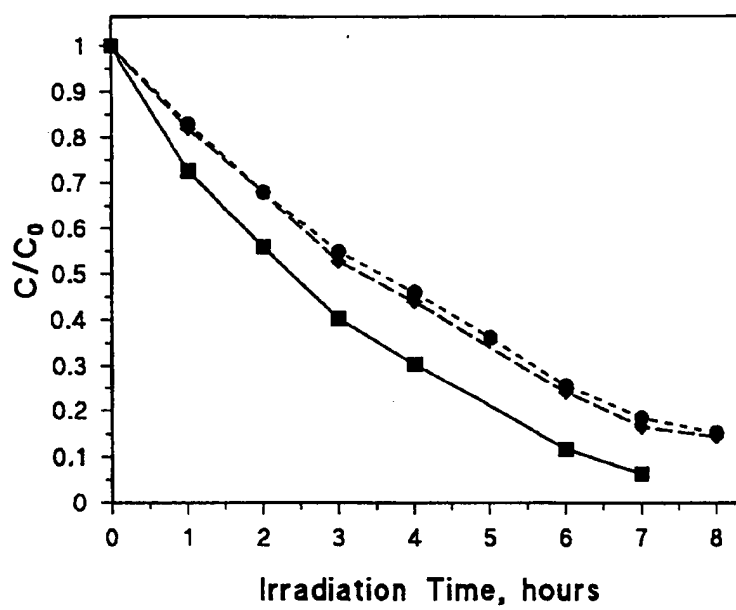


Figure 7



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 00 20 3953

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	DATABASE WPI Section Ch, Week 200116 Derwent Publications Ltd., London, GB; Class D22, AN 2001-150734 XP002165611 & JP 2000 273355 A (MITSUBISHI MATERIALS CORP), 3 October 2000 (2000-10-03) * abstract *		B01J35/00 B01J21/06 B01J37/02
A	DE 198 58 933 A (HARTWIG GERALD) 15 June 2000 (2000-06-15)		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.7) B01J B05D
Place of search THE HAGUE		Date of completion of the search 19 April 2001	Examiner Thion, M
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date O: document cited in the application L: document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 20 3953

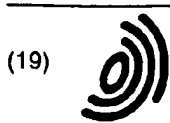
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19-04-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2000273355 A	03-10-2000	NONE	
DE 19858933 A	15-06-2000	NONE	

EP 00 20 3953

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82



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(11) **EP 1 302 234 A1**

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
16.04.2003 Bulletin 2003/16

(51) Int Cl.7: **B01D 53/86**, B01J 19/12,
B01D 35/10

(21) Application number: **02021779.0**

(22) Date of filing: **26.09.2002**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
IE IT LI LU MC NL PT SE SK TR**
Designated Extension States:
AL LT LV MK RO SI

(72) Inventors:
• Nishii, Yoshikazu, Hoya-Schott Corporation
Shinjuku-ku, Tokyo 160-0023 (JP)
• Arai, Souji, Hoya-Schott Corporation
Shinjuku-ku, Tokyo 160-0023 (JP)

(30) Priority: **27.09.2001 JP 2001335723**

(74) Representative: **HOFFMANN - EITLE
Patent- und Rechtsanwälte
Arabellastrasse 4
81925 München (DE)**

(71) Applicant: **Hoya- Schott Corporation
Tokyo 160-0023 (JP)**

(54) **Light-transmittable linear photocatalytic filter material, filter to which the material is applied, and process for production thereof**

(57) Light-transmittable linear photocatalytic filter material that can be arranged in parallel in the longitudinal direction without causing a filter to have the form of a barrel when the filter is made of a bundle of a number of such photocatalytic filter materials, each comprising a light-transmittable linear material, a number of particulate materials bonded to an outer side surface of the light-transmittable linear material and a photocatalyst layer formed on said outer side surface

and said number of particulate materials, wherein a maximum value of heights from said outer side surface to said photocatalyst layer in a central region of said light-transmittable linear material in the longitudinal direction is smaller than a maximum value of heights from said outer side surface to said photocatalyst layer in regions of both ends thereof.

EP 1 302 234 A1

Description

Background of the Invention

Field of the Invention

[0001] The present invention relates to a light-transmittable linear photocatalytic filter material having a long and narrow light-transmittable linear material and a number of particulate materials provided on an outer surface of the linear material, and further having a photocatalytic layer formed on or above an outer surface of the linear material and the number of particulate materials; a filter formed of such light-transmittable linear photocatalytic filter materials; and a process for producing the above filter material.

Prior Art

[0002] A photocatalyst is a material that exhibits functions of sterilization, antimicrobial activity, decomposition, deodorization, non-soiling, non-fogging, and the like when exposed to light. When titanium dioxide, a typical example of the photocatalyst, is exposed to light, the titanium dioxide causes an intense redox reaction on its surface to decompose a substance that is in contact with the surface. For example, when the above substance is an organic substance, the organic substance is decomposed into carbon dioxide gas and water. The photocatalyst decomposes, for example, environmental pollutants such as microorganisms, virus, malodorous substances, dioxin, trichloroethylene, etc., and endocrine-disturbing chemicals that may cause a sick building syndrome.

[0003] Attempts are being made to utilize the above photocatalysis for a filter and apply the filter to disposing of various liquids, disposing of various gases and environmental cleaning.

[0004] For providing a high-performance photocatalytic filter at a less expensive price, there is proposed a photocatalytic filter material having a filter base material formed by bonding particulate materials to a surface of a long and narrow light-transmittable linear material to form projections and a photocatalyst layer formed on the filter base material (JP-A-10-71312).

[0005] When a large number of such photocatalytic filter materials are bundled with aligning their ends on each side to constitute a photocatalytic filter, gaps are formed among the filter materials adjacent side by side owing to the presence of the above projections, so that a fluid to be disposed of can be allowed to flow through the above gaps. Further, passage spaces forming the above gaps do not easily change with the passage of time or are stabilized, so that the photocatalytic filter can maintain performances as a filter for a long period of time.

[0006] In the above photocatalytic filter, one end surface or each end surface of a bundle formed of a number

of photocatalytic filter materials is provided with a light incidence portion, and light such as ultraviolet ray is allowed to enter the light incidence portion and is propagated inside the photocatalytic filter materials. Since the photocatalyst layer (e.g., titanium dioxide) has a higher refractive index than the linear material (e.g., glass fiber), the propagated light above has no components that undergo total reflection, so that it leaks into the photocatalyst layer.

[0007] When an inorganic adhesive containing silica as a main component is used as an adhesive for bonding particulate materials as projections to outer side surfaces of the light-transmittable linear materials, the refractive index of the adhesive satisfies the condition of total reflection since it is equivalent to, or slightly lower than, the refractive index of the light-transmittable linear materials, so that no light leaks into the photocatalyst layer. Since, however, microscopic pores are formed in an interface between the light-transmittable linear materials and the adhesive after the adhesive is baked, there occurs light that leaks into the photocatalyst layer through the pores as base points. Therefore, the light that enters the light incidence portion is not propagated far but gradually leaks into the photocatalyst layer, and the photocatalyst layer is irradiated with the light that has leaked into it.

[0008] On the other hand, a fluid to be disposed of is allowed to flow "uniformly" through the passage of gaps of a bundle of a number of the photocatalytic filter materials, whereby the photocatalytic filter traps contaminants contained in the fluid to be disposed of, with the surface of the photocatalyst layer. The photocatalyst layer is irradiated with the above light that leaks into it, whereby the trapped contaminants are decomposed by photocatalysis.

[0009] It is expected that the efficiency of the photocatalysis is increased with an increase in the number of photocatalytic filter materials bundled. In reality, however, when the number of the photocatalytic filter materials bundled comes to be thousands, tens of thousands or more, there is caused another new problems.

[0010] For example, as shown in Fig. 11, a number of quartz glass spheres 2 (average particle diameter; 50 μm) as particulate materials are bonded to an outer surface of a fiber 1 made of glass as a long and narrow light-transmittable linear material with an adhesive. Further, a titanium dioxide layer 4 (thickness; 2 μm) is formed on the above number of quartz glass spheres 2 and an outer surface of the fiber 1 made of quartz glass by a known dipping method, to prepare a glass fiber photocatalytic filter material 90. About 70,000 photocatalytic filter materials 90 are bundled to obtain a photocatalytic filter. In the thus-obtained photocatalytic filter, the following abnormal phenomenon takes place.

[0011] As shown in Fig. 12, when such photocatalytic filter materials 90 are bundled with their ends on each side aligned, and housed in a cylindrical case 5 made of aluminum (internal diameter; 70 mm ϕ , a length; 200

mm) to constitute a photocatalytic filter 91, the photocatalytic filter 91 has the form of a barrel as shown in Fig. 12. The above "form of a barrel" means that photocatalytic filter materials 90 positioned on outer side surface of central portion of the photocatalytic filter 91 swell outwardly in a convex form. As shown in Fig. 12, the middle portions of the photocatalytic filter materials 90 are in close contact with the internal side surface of the cylindrical case 5, and a space portion 7 occurs near an opening on each side of the photocatalytic filter.

[0012] The photocatalytic filter 91 sufficiently performs as a filter only when a fluid to be disposed of is allowed to flow "uniformly" through the passage of gaps formed by particulate materials 2 among the photocatalytic filter materials 90 of the photocatalytic filter 91 formed by bundling a number of the photocatalytic filter materials 90 with aligning their ends on each side. In the above space portion 7, however, the flow of the fluid abnormally increases in amount, and the flow comes to be non-uniform, so that the photocatalytic filter cannot sufficiently work as a filter.

[0013] As shown in Fig. 13, when an overflow state of a water stream 8 is observed in a test in which a photocatalytic filter formed of a number of photocatalytic filter materials 90 is allowed to stand upright and the water is allowed to flow upwardly in a stream 8 (flow rate: 2 liters/minute), water stream 8 above the above space portion 7 rapidly flows to cause a standing portion 6. The above test result shows the above abnormal phenomenon of a fluid caused by the space portion 7.

Summary of the Invention

[0014] It is therefore an object of the present invention to provide light-transmittable linear photocatalytic filter materials that can be arranged in parallel in the longitudinal direction without causing a filter to have the form of a barrel when the filter is made of a bundle of a number of such photocatalytic filter materials; a filter made of the above photocatalytic filter materials, and a process for the production of the above photocatalytic filter materials.

[0015] According to a first aspect of the present invention for achieving the above object, there is provided a light-transmittable linear photocatalytic filter material comprising a light-transmittable linear material, a number of particulate materials bonded to an outer side surface of the light-transmittable linear material and a photocatalyst layer formed on said outer side surface and said number of particulate materials,

said light-transmittable linear photocatalytic filter material being for the production of a light-transmittable linear photocatalytic filter in which light enters one end or both ends of said light-transmittable linear material, propagates inside said light-transmittable linear material and leaks into said photocatalyst layer and said photocatalyst layer is irradiated with the leaked light, characterized in that:

a maximum value of heights from the outer side surface of the linear material to the surface of the photocatalyst layer in a central region of said light-transmittable linear material in the longitudinal direction is smaller than a maximum value of heights from the outer side surface of the linear material to the surface of the photocatalyst layer in regions of both ends thereof.

[0016] According to a second aspect of the present invention for achieving the above object, there is provided a light-transmittable linear photocatalytic filter material that is according to the first aspect of the present invention and also satisfies requirements that the central region of the outer surface of said light-transmittable linear material in the longitudinal direction has a length in the range of from 20 % to 60 % based on the total length of said outer surface; that each end region of the outer surface of said light-transmittable linear material in the longitudinal direction has a length in the range of from 20 % to 40 % based on said total length; and that said particulate materials distributed in said central region has a lower density than said particulate materials distributed in each end region.

[0017] According to a third aspect of the present invention for achieving the above object, there is provided a light-transmittable linear photocatalytic filter comprising a bundle of a large number of light-transmittable linear photocatalytic filter materials according to the first or second aspect of the present invention.

[0018] According to a fourth aspect of the present invention for achieving the above object, there is provided a process for producing light-transmittable linear photocatalytic filter materials each of which is made of a long and narrow linear material, a number of particulate materials that are bonded to an outer side surface of the linear material in a predetermined distribution density, and a photocatalyst layer formed on said outer surface and said particulate materials, comprising the steps of:

mixing a number of light-transmittable linear materials, a number of particulate materials and a predetermined amount of an adhesive to temporarily bond said light-transmittable linear materials and said particulate materials,

housing said light-transmittable linear materials and said particulate materials that are temporarily bonded, in a container having a pair of facing net-shaped surfaces,

placing weights having a bottom having a predetermined area and having a predetermined loading weight on central portions of said net-shaped surfaces to press said light-transmittable linear materials and said particulate materials, and

rocking or vibrating said container in a state where said light-transmittable linear materials and said particulate materials are pressed, for a predetermined time period, to rub off particulate materials

on a central region of said temporarily bonded linear materials in the longitudinal direction.

Brief Description of Drawings

[0019]

Fig. 1 is a cross-sectional view of a photocatalytic filter material in Example 1, taken along the longitudinal direction.

Fig. 2 is a cross-sectional view of a photocatalytic filter material in Example 2, taken along the longitudinal direction.

Fig. 3 is a vertical cross-sectional view of end region of each of the photocatalytic filter materials in Figs. 1 and 2.

Fig. 4 is a cross-sectional view of an end region of each of the photocatalytic filter materials shown in Figs. 1 and 2 in the longitudinal direction.

Fig. 5 is a cross-sectional view of a photocatalytic filter formed by housing a bundle of approximately 70,000 photocatalytic filter materials shown in each of Figs. 1 and 2 in a cylindrical case.

Fig. 6 is a diagram showing water stream when water is allowed to flow through the photocatalytic filter shown in Fig. 5.

Fig. 7 shows a container that houses a mixture of a number of photocatalytic filter materials, a number of particulate materials and an adhesive, which are temporarily bonded, and having a pair of net-shaped surfaces facing each other upwardly and downwardly, and a state where weights are placed on a pair of the net-shaped surfaces to apply a load.

Fig. 8 is a diagram showing the structure of one example of a photocatalytic filter device using the photocatalytic filter of the present invention.

Fig. 9 is a diagram showing an apparatus for evaluating performances of the photocatalytic filter device shown in Fig. 8.

Fig. 10 shows a difference in the removal ratio of benzene between a photocatalytic filter device using the photocatalytic filter materials in Example 1 of the present invention and a photocatalytic filter device using conventional photocatalytic filter materials in Comparative Example 1.

Fig. 11 is a cross-sectional view of a conventional photocatalytic filter material in the longitudinal direction.

Fig. 12 is a cross-sectional view of a photocatalytic filter formed by housing a bundle of approximately 70,000 conventional photocatalytic filter materials in a cylindrical case.

Fig. 13 is a diagram showing water stream when water is allowed to flow through the photocatalytic filter shown in Fig. 12.

Preferred Embodiments of the Invention

[0020] In light-transmittable linear photocatalytic filter material according to the first aspect of the present invention, the "particulate materials" refers to particles having a spherical, oval or undefined form. Spherical particles are preferred.

[0021] The "light-transmittable linear material" refers to a fiber-shaped or rod-shaped linear material that transmits light. Any linear material may be used so long as its internal transmittance of light such as ultraviolet ray or visible light is at least 90 %, preferably at least 96 % per 10 cm of a length of the linear material at an excitation wavelength of the photocatalyst used. Specific examples of the light-transmittable linear material include a quartz glass fiber and multi-component glass fibers made of silicon dioxide as a main component such as fibers of a silicate glass having a low alkali content, an aluminosilicate glass, a borosilicate glass and alkali-free silicate glass.

[0022] The long and narrow light-transmittable linear material can be any one so long as it has a size sufficient to retaining its mechanical strength and is as narrow as possible. For example, a light-transmittable linear material having a diameter of 1 to 500 μm is preferred, and a light-transmittable linear material having a diameter of 10 to 200 μm is more preferred. The above limitations are employed for the following reasons. When the above diameter is smaller than 1 μm , the mechanical strength of the linear material itself is low, and when its end portion is used as a light incidence portion, the efficiency of light incidence is low. When the above diameter is larger than 500 μm , it is difficult to secure surface areas of such linear materials that are bundled to constitute a filter, and such a filter is not sufficient for practical use. The length of the light-transmittable linear material and the number of such light-transmittable linear materials to be bundled are not critical and can be selected as required depending upon purposes.

[0023] When the above particulate materials are spherical (average particle diameter d) and when the long and narrow light-transmittable linear material has the form of a column (diameter D), the particle diameter d of the particulate materials is preferably in the range of 4 % to 70 %, more preferably 25 to 60 %, based on the diameter D of the light-transmittable linear material. It is preferred to use particulate materials having diameters of which the variability is as small as possible, and for example, the variability (difference) of the diameters is preferably in the range of ± 30 % of an average particle diameter d when the average particle diameter d is taken as a central value.

[0024] The reason therefor is as follows. When filter materials are bundled to constitute a filter, and when the particle diameter d of the particulate materials is smaller than 4 % of diameter D of the light-transmittable linear material, no large space of gaps can be formed among the filter materials, and the pressure loss increases.

When the particle diameter d of the particulate materials is larger than 70 % of diameter D of the light-transmittable linear material, the strength of adhesion of the particulate materials to the light-transmittable linear materials is extremely low, so that no stable filter can be obtained. When the variability of the particle diameters is outside ± 30 % of the central value as an average particle diameter d , the maximum value of heights from an outer surface of the light-transmittable linear materials to the photocatalyst layer on a number of the particulate materials varies to a great extent, and no uniform gaps can be formed, so that no uniform stream of a fluid can be formed. Such a filter therefore cannot be practically used.

[0025] The photocatalyst layer is typically a layer of titanium dioxide. Besides it, the photocatalyst layer includes layers formed of substances having photocatalysis such as barium titanate, strontium titanate, sodium titanate, zirconium dioxide, cadmium sulfide and α - Fe_2O_3 . The thickness of the photocatalyst layer is preferably approximately 0.1 μm to 10 μm . When the above thickness is smaller than 0.1 μm , the amount of light absorption is small, and it is difficult to create many catalytic activation sites. When the above thickness is larger than 10 μm , light cannot reach an outermost surface (reaction surface) of the photocatalyst layer since the photocatalyst layer is irradiated in a manner that the reverse surface of the photocatalyst layer is irradiated. Hence, no catalytic activation site can be formed. In any one of these cases, it is difficult to put such a filter to practical use.

[0026] The above-described light-transmittable linear materials have a refractive index of approximately 1.45 to 1.65. The refractive index of the material constituting the photocatalyst layer at an excitation wavelength can be assumed to be 2.0 or more although it is difficult to measure such a value accurately since light absorption takes place. In this case, light that enters the light-transmittable linear material does not satisfy the condition of total reflection, so that it leaks into the photocatalyst layer and the photocatalyst layer can be irradiated with the light that leaks.

[0027] In the light-transmittable linear photocatalytic filter material according to the first aspect of the present invention, when a number of such light-transmittable linear photocatalytic filter materials having a number of particulate materials bonded to an outer side surface thereof are bundled to constitute a filter, space portions where the above number of particulate materials are not present are formed as gaps among the light-transmittable linear photocatalytic filter materials, and the gaps constitute a passage for a fluid to be disposed of. When a fluid to be disposed of is allowed to flow through the gaps (passage) among the light-transmittable linear materials of the photocatalytic filter materials, the fluid flows substantially uniformly, and the light-transmittable linear photocatalytic filter materials work as a filter.

[0028] In the light-transmittable linear photocatalytic

filter material according to the first aspect of the present invention, further, a maximum value of heights from the outer side surface of the light-transmittable linear material to the above photocatalyst layer in a central region of the light-transmittable linear material in the longitudinal direction is smaller than a maximum value of heights from the outer side surface to the above photocatalyst layer in regions of both ends thereof. When a number of such light-transmittable linear photocatalytic filter materials are bundled to constitute a filter, therefore, the bundle (filter) can have the form of a Japanese hand drum or tsuzumi (having an inwardly curved form in a central region of a side surface, the form of a filter having an inwardly curved (concave) side surface in a central region) unlike the above form of a barrel, so that the light-transmittable linear photocatalytic filter materials can be aligned substantially in parallel with one another.

[0029] In the light-transmittable linear photocatalytic filter material according to the second aspect of the present invention, the light-transmittable linear photocatalytic filter material according to the first aspect of the present invention satisfies the requirements that the central region of the outer surface of said light-transmittable linear material in the longitudinal direction has a length in the range of from 20 % to 60 % based on the total length of said outer surface; that each end region of the outer surface of said light-transmittable linear material in the longitudinal direction has a length in the range of from 20 % to 40 % based on said total length; and that said particulate materials distributed in said central region has a lower density than said particulate materials distributed in each end region. When a number of such light-transmittable linear photocatalytic filter materials are bundled to constitute a filter, therefore, the filter materials can be aligned in the longitudinal direction with a higher parallelism, a fluid to be disposed of can be allowed to flow more uniformly, and the filter exhibits its functions more efficiently.

[0030] The reason why the length of central region of the outer surface of the light-transmittable linear material in the longitudinal direction is determined to be in the range of from 20 % to 60 % based on the total length of said outer surface in the longitudinal direction is as follows. When the above length of central region of the outer surface of the light-transmittable linear material is smaller than 20 % of the above total length, a bundle of a number of such filter materials may possibly have the above form of a barrel. When the above length of central region of the outer surface of the light-transmittable linear material is larger than 60 % of the above total length, the parallelism of the filter materials in the longitudinal direction can be maintained at a good level, but the mechanical strength of the filter materials may possibly decrease.

[0031] The reason why the length of each end region of the outer surface of the light-transmittable linear material in the longitudinal direction is determined to be in the range of from 20 % to 40 % based on the above total

length is as follows. The length of each end region corresponds to a length of one of two end (backward end and forward end) regions other than the above central region. When the length of each end region of the outer surface of the light-transmittable linear material is smaller than 20 % of the above total length, the mechanical strength of the filter materials may possibly be low. When the above length is larger than 40 %, a bundle of a number of such filter materials may possibly have the above form of a barrel.

[0032] In the operation of bundling filter materials, broken pieces from linear materials or particulate materials or foreign matter may be sometimes contained in the central region of the filter materials since they are too small (equivalent to, or smaller than the size of the particulate materials) and overlooked. In this case, when a number of conventional filter materials are bundled to constitute a filter, the bundled filter materials form a convex portion greater than the convex portion of the barrel form shown in Fig. 12, and a space portion that appears near an opening on each end portion is greater than the space portion 7 shown in Fig. 12. The light-transmittable linear photocatalytic filter material according to the present invention is significant as follows. When the filter materials of the present invention are bundled to constitute a filter, the filter materials can maintain their parallelism in the longitudinal direction even in the above case.

[0033] The light-transmittable linear photocatalytic filter according to a third aspect of the present invention comprises a bundle of a large number of light-transmittable linear photocatalytic filter materials according to the first or second aspect of the present invention. As a filter case for placing the filter materials therein, tubular cases such as a cylindrical case and a case having the form of a polygonal pillar such as a square pillar or a hexagonal pillar are preferred. The internal diameter of the filter case is determined depending upon the number of the filter materials that are to be bundled. As a material for the filter case, metals such as aluminum and brass and plastics are preferred. The form and the material of the filter case shall not be limited thereto and can be determined as required in designing.

Preferred Embodiments of the Invention

[0034] Figs. 1 and 2 show cross-sectional view, taken in the longitudinal direction, of light-transmittable linear photocatalytic filter materials 100 and 101 in Examples 1 and 2 of the present invention. In each of Figs. 1 and 2, a glass fiber 1 itself is the same as the glass fiber shown in Fig. 11. The glass fiber 1 has a diameter of 125 μm and a length of 200 mm. The glass fiber 1 has an internal transmittance of 97 % at a wavelength of 365 nm per 10 cm thereof and has a refractive index (at wavelength of 365 nm) of approximately 1.58.

[0035] Quartz glass spheres 2 shown in Figs. 1 and 2 are the same as those shown in Fig. 11 in that they

have an average particle diameter of 50 μm and that a number of quartz glass spheres 2 which are stacked on an outer side surface of the glass fiber to form one stage or two or more stages on the outer side surface are distributed as aggregates each of which is formed of two or more spheres adjacent side by side as a unit. The distribution of these spheres 2 differs from that shown in Fig. 11 as follows. Incidentally, a titanium dioxide layer 4 (thickness; 2 μm) formed as a photocatalyst layer on an outer side surface of the glass fiber 1 and the quartz glass spheres 2 bonded to an outer side surface thereof with an adhesive 3 (see Figs. 3 and 4) is the same as that shown in Fig. 11, so that a detailed explanation thereof is omitted.

[0036] That is, as shown in Fig. 1, quartz glass spheres 2 are not present in the central region of the glass fiber 1 in the longitudinal direction, and quartz glass spheres 1 that are distributed on each end region are stacked to constitute one stage or two stages. In this case, the maximum value of heights from an outer side surface of the glass fiber 1 to the titanium dioxide layer 4 in the central region is 2 μm , which is the thickness of the titanium dioxide. The maximum value of heights from an outer side surface of the glass fiber 1 to the titanium dioxide layer 4 in each end region corresponds to a total (approximately 102 μm) of a height of quartz glass spheres 2 forming the two stages (approximately 100 μm) and the thickness (2 μm) of the titanium dioxide layer 4. Therefore, the photocatalytic filter material 100 having a central region and each end region is formed such that the central region has a smaller height and that the end regions have a larger height.

[0037] In the above filter material 100, the length of the central region thereof is determined to be 60 ± 5 mm, which corresponds to 30 % of the total length (200 mm) of the glass fiber 1, the length of each end region of the glass fiber 1 in the longitudinal direction is determined to be 70 ± 5 mm, which corresponds to 35 % of the total length, and as described above, the quartz glass spheres 2 are not present in the central region, and aggregates of the quartz glass spheres 2 forming one stage or two stages stacked are scattered in each end region, so that the density of the quartz glass spheres 2 distributed in the central region is lower than the density of the quartz glass spheres 2 distributed in each end region.

[0038] Further, with reference to the above Fig. 1, Fig. 3 that is a cross-sectional view of an end region of the filter material 100 taken at right angles with the longitudinal direction, and Fig. 4 that is a cross-sectional view of part of an end region taken along the longitudinal direction and shows a distribution of the quartz glass spheres, the quartz glass spheres 2 are bonded and fixed to an outer side surface of each end region of the glass fiber 1, such that aggregates formed of two, three or more quartz glass spheres 2 bonded side by side are constituted as a unit. Therefore, the bonding strength of the quartz glass spheres 2 to an outer surface of the

glass fiber 1 is high as compared with the bonding strength of such quartz glass spheres that bond to the above outer surface one by one when the same adhesive is used, and the adhesion of the titanium dioxide layer 4 formed thereon is also enhanced.

[0039] When a number of such glass fiber photocatalytic filter materials 100 are bundled to constitute a filter, the space of gaps formed by the distribution of the above quartz glass spheres 2 is stabilized and is stable against a change with the passage of time, so that the requirement of uniform flow of a fluid through the filter is satisfied.

[0040] In a photocatalytic filter material 101 shown in Fig. 2, all of quartz glass spheres 2 in a central region of a glass fiber 1 in the longitudinal direction form one stage, the quartz glass spheres 2 are bonded and fixed to an outer surface of the glass fiber 1 and distributed such that aggregates formed of two, three or more quartz glass spheres 2 bonded side by side are constituted as a unit, and quartz glass spheres 2 in each end region are distributed such that aggregates similar to the above aggregates are constituted as a unit, and quartz glass spheres 2 are also distributed such that aggregates formed of one or two stages are constituted.

[0041] The above photocatalytic filter material 101 therefore satisfies the requirement of uniform flow of a fluid through a filter. The maximum value of heights from an outer side surface of the glass fiber 1 to a titanium dioxide layer 4 in a central region corresponds to a total (52 μm) of a thickness of one stage (50 μm) of the quartz glass spheres 2 and the thickness (2 μm) of the titanium dioxide layer 4, and the maximum value of heights from an outer side surface of the glass fiber 1 to the titanium dioxide layer 4 in each end region corresponds to a total (approximately 102 μm) of the height (approximately 100 μm) of two stages of the quartz glass spheres 2 and the thickness (2 μm) of the titanium dioxide layer 4, so that the photocatalytic filter material 101 having a central region and each end region is formed such that the central region has a smaller height and that the end regions have a larger height.

[0042] In the above photocatalytic filter material 101, the length of the central region is determined to be 100 ± 5 mm, which corresponds to 50 % of the total length (200 mm) of the glass fiber 1 in the longitudinal direction, the length of each end region of the glass fiber 1 in the longitudinal direction is determined to be 50 ± 5 mm, which corresponds to 25 % of the total length. The density of the quartz glass spheres 2 distributed in the central region is determined to be lower than the density of the quartz glass spheres 2 distributed in each end region.

[0043] As shown in Fig. 5, 70,000 photocatalytic filter materials 100 or 101 are bundled, inserted into a cylindrical case 5 made of aluminum (internal diameter 70 mm, length 200 mm) and fixed therein. End surfaces thereof on each side are aligned and polished, and then they are to be used as a light incidence portion, whereby

a photocatalytic filter 102 or 103 is completed.

[0044] The thus-obtained photocatalytic filter 102 or 103 was subjected to the above water stream test, and as shown in Fig. 6, water stream 8 (flow rate: 2 liters/minute) was observed for an overflow on an upper plane thereof. As a result, it was found that water smoothly flowed at a uniform flow rate without causing the standing portion 6 as shown in Fig. 13.

[0045] The process for the production of the above photocatalytic filter materials 100 will be explained below.

(Temporary bonding step)

[0046] First, there are provided 70,000 glass fibers (diameter; 125 μm , length; 200 mm, trade name "PFG1 Glass Fiber" supplied by HOYA-SCHOTT" and 40 g of quartz glass spheres 2 (average particle diameter; 50 μm , trade name "SSV-43" supplied by K.K. Tatsumori), and they are encased in a proper container with a cover (width; 80 mm, length; 220 mm, depth; 60 mm, trade name "Natural Pack" supplied by K.K. Nishiyama Kagaku).

[0047] Then, 40 ml of an adhesive (trade name "FJ-803" supplied by Tokiwa Denki K.K.) is poured into the container with the above glass fibers 1 and quartz glass spheres in it, and the container was covered. The container was moved backward and forward repeatedly (e.g., stroke; 80 mm, five strokes/minutes) to stir them, whereby there is obtained a properly bonded mixture of the glass fibers 1, the quartz glass spheres 2 and the adhesive. The above mixture is in a bonding state in which the adhesive adheres to the glass fibers 1 and the quartz glass spheres 2 while retaining a proper flowability since it is not yet cured, and the glass fibers 1 and the quartz glass spheres 2 are temporarily bonded to one another through the adhesive.

(Step of adjusting distribution of particulate materials)

[0048] Then, the properly bonded mixture obtained in the temporary bonding step is placed in a container 9 (width; 100 mm, length; 260 mm, depth; 80 mm) having a net 11 spread in a bottom portion (width; 100 mm, length; 260 mm) and a net-shaped cover 10 as shown in Fig. 7. The net-shaped cover 10 is placed on the container 9. The net-shaped cover 10 and the net 11 in the bottom of the container 9 form a pair of facing mesh surfaces.

[0049] The net-shaped cover 10 and the net 11 in the bottom of the container 9 work as mesh surfaces. Corners-rounded acryl blocks 12 and 13 (width; 30 mm, length; 60 mm, height; 40 mm, weight; about 80 g) as weights are placed on central portions of the nets one on each, to apply a load thereon. The nets 10 and 11 are brought into a state where the central portions of the nets 10 and 11 are pressed inwardly into the container 9 by approximately 5 mm.

[0050] In the above pressed state, the container 9 is rocked (or may be vibrated instead; "rock" or "rocking" hereinafter may be replaced with "vibrated" or "vibration" hereinafter). In the rocking, the container 9 is moved backward and forward (e.g., stroke; 100 mm, 4 strokes/second) such that the bonded mixture inside the container 9 are moved in an accelerated motion in the width direction of the container.

[0051] During the above accelerated motion, the blocks 12 and 13 exert a load particularly on a number of the glass fibers 1 facing the surfaces (width; 30 mm, length; 60 mm) of the blocks 12 and 13. The length (60 mm) of each of the blocks 12 and 13 corresponds to the central region of the glass fibers 1 in the longitudinal direction. Of the quartz glass spheres 2 temporarily bonded to outer side surfaces of the glass fibers 1 with the adhesive, therefore, the quartz glass spheres 2 present in the central region of the glass fibers 1 in the longitudinal direction are rubbed off.

[0052] Then, hot air (80°C) is blown through the net 10 or 11 of the container 9 to dry the adhesive. By the blowing, the quartz glass spheres 2 alone are bonded to outer side surfaces of the glass fibers 1 while the glass fibers 1 are not bonded to one another. The above rocking, the above loading with the blocks and the above blowing with hot air are continued until the adhesive is cured (e.g., for 10 minutes).

[0053] As a result, the quartz glass spheres 2 bonded to outer surfaces of the glass fibers 1 have the following distribution density. In the entire length (200 mm) of the outer side surfaces of the glass fibers 1, the density of the quartz glass spheres 2 distributed in the central region (60 mm) of the glass fibers 1 in the longitudinal direction is low, and the density of the quartz glass spheres 2 distributed in each end region (70 mm) is high. The length of the central region of the glass fibers 1 can be adjusted on the basis of dimensions of the loading blocks 12 and 13, and the amount of the quartz glass spheres 2 that are to be rubbed off can be adjusted on the basis of a load (weight) of the blocks 12 and 13, the speed of the repeated backward and forward movement and the operation time period. By the above procedures, the quartz glass spheres 2 having a desired distribution density can be scattered, and the numbers of stacks of the quartz glass spheres 1 in desired regions, that is, heights from the outer side surfaces of the glass fibers 1, can be adjusted.

[0054] The above-explained step of adjusting the particulate materials is a simple step in which bonded mixture of glass fibers, quartz glass spheres and an adhesive are rocked while exerting a load on a region where the distribution density of the quartz glass spheres is to be decreased in surfaces of the glass fibers. Therefore, the above step is excellent in mass-productivity and suitable particularly for producing filters each of which is constituted of a larger number of filter materials. Further, since no excess external force is exerted on the glass fibers, there is almost no possibility of the glass fibers

being damaged, and the above step serves to the production of filters at goods yields.

(Heating step)

[0055] Then, the glass fibers with a number of the quartz glass spheres bonded thereto, obtained in the above step of adjusting distribution of particulate materials, are taken out of the container 9. Further, for improving the adhesion between the outer side surfaces of the glass fibers 1 and the quartz glass spheres 2, the glass fibers with a number of the quartz glass spheres bonded thereto are placed in a heating furnace and heated (e.g., at 300°C for 2 hours).

(Step of forming photocatalyst layer)

[0056] A titanium dioxide layer 4 is formed on outer side surfaces of the glass fibers with a number of the quartz glass spheres bonded thereto, obtained by the above heating step, by a known dipping method or a blow away method (see JP-A-2000-5691). In this embodiment, a titanium dioxide layer 4 having a thickness of 2 μ m was formed by a dipping method.

[0057] As shown in Fig. 1, the titanium dioxide layer 4 is formed on the outer surfaces of the glass fibers 1 and on surfaces of the quartz glass spheres 2 bonded to outer surfaces of the glass fibers 1. In the above manner, a number of (approximately 70,000) photocatalytic filter materials of the glass fibers with the quartz glass spheres bonded thereto and with the photocatalyst layer 4 formed thereon can be simultaneously produced.

(Step of forming photocatalytic filter)

[0058] As shown in Fig. 5, ends of a number of the photocatalytic filter materials 100 obtained in the above step of forming photocatalyst layer are aligned on each side, and the photocatalytic filter materials 100 are bundled. The bundled photocatalytic filter materials 100 are encased and inserted in a proper cylindrical case 5 (internal diameter; 70 mm ϕ , length; 200 mm) made of aluminum, to give a photocatalytic filter 102 or 103.

[0059] For simplification of explanations of the present invention, the lengths of end portions of the glass fibers 1 on each side which end portions are cut and/or polished for providing a light incidence portion have not been taken account of with regard to the length of the glass fibers 1 and the lengths of the containers and tools used for production concerned hereinabove. For producing a practical photocatalytic filter, the length of the glass fibers 1 is determined beforehand to be longer by taking account of a margin necessary for the cutting and polishing, and the lengths of the containers and tools used for production concerned are determined so as to meet with the above length.

[0060] Fig. 8 shows an example of a photocatalytic filter device 200 to which a photocatalytic filter 102 ob-

tained by the above production method is applied. The photocatalytic filter device 200 comprises the photocatalytic filter 102 and ultraviolet light sources 21 and 22 (wavelength; 365 nm, trade name "EX250" supplied by HOYA-SCHOTT).

[0061] Around the photocatalytic filter 102, there are provided a filter case 14 housing the above photocatalytic filter materials 100, flange portions 15 and 16 formed on both sides of the filter case 14, a fluid inlet 17 and a fluid outlet 18 provided in side portions of the flange portions 15 and 16, and glass windows 19 and 20 ("Optical Glass F2" supplied by HOYA-SCHOTT, that can cut a wavelength of 300 nm or shorter) for constituting open end surfaces on both sides and transmitting incidence light.

[0062] Ultraviolet light sources 21 and 22 are disposed to face the glass windows 19 and 20, and ultraviolet lights L_0 and L_1 emitted therefrom enter light incidence portions formed on both ends the photocatalytic filter 102 through the glass windows 19 and 20 and propagate in a number of the filter materials 100 constituting the photocatalytic filter 102. The lights leak into the titanium dioxide layers formed on outer side surfaces thereof to irradiate the titanium dioxide layers, whereby the filter produces photocatalysis.

[0063] A fluid to be disposed of is introduced through the fluid inlet 17 and allowed to flow through fluid passages of gaps formed among adjacent filter materials with a number of quartz glass spheres 2 bonded to outer side surfaces of a number of the photocatalytic filter materials 100 constituting the photocatalytic filter 102, and contaminants in the fluid are decomposed and removed by the above photocatalysis of the titanium dioxide layers 4. The fluid is discharged through the fluid outlet 18.

[0064] For testing the above photocatalytic filter device 200 for performances, there was prepared an apparatus 300 for evaluating the gas removal performance of a photocatalytic filter shown in Fig. 9. The performance evaluating apparatus 300 has a gas container 24 containing a disposal gas 23 containing contaminants; a pure air container 26 containing pure air 25; a mass flow controller 27 for controlling the flow rate of the disposal gas 23; a humidity controller 28 for controlling the humidity of the pure air 25; a mass flow controller 29 for controlling the flow rate of the pure air; a mixer 30 for mixing the disposal gas 23 and the pure air 25 controlled through the above mass flow controllers 27 and 29 to dilute the disposal gas 23 to prepare a disposal gas having a predetermined concentration; a buffer tank 31 for storing the disposal gas from the mixer 30 once and bringing it to an ordinary pressure state; the above photocatalytic filter device 200 that is to produce photocatalysis when the mixture gas from the above buffer tank 31 is introduced; a pump 32 for introducing the above mixture gas into the above photocatalytic filter device 200 at a predetermined flow rate; and a flow meter 33 for measuring the flow of the mixture gas.

[0065] The above members were connected with

pipes and tubes made of stainless steel. On the gas inlet side and the gas outlet side of the photocatalytic filter device 200, the mixture gas was detected for gas concentrations with detectors (gas chromatography "FC-14B" supplied by Shimadzu Corporation). The humidity was adjusted to 50 %RH as a humidity at a temperature of 25°C. The ultraviolet intensity was adjusted to 8 mW/cm² on each end surface of the fiber bundle, and distances between emission ends of light guides made of quartz glass and connected to the ultraviolet light sources 21 and 22 and incidence ends of the photocatalytic filter 102 are adjusted and fixed. The flow rate was adjusted to 11 liters/minute on the basis of an open/close state of a valve attached to the pump 32 and fixed.

[0066] There was prepared a photocatalytic filter device having the constitution of the above photocatalytic filter device 200 but using a photocatalytic filter 91 formed by bundling glass fiber photocatalytic filter materials 90 in Comparative Example 1 shown in Fig. 11 and Fig. 12. Further, there was prepared a photocatalytic filter device having the constitution of the above photocatalytic filter device 200 and using a photocatalytic filter 102 formed by bundling glass fiber photocatalytic filter materials in Example 1. For forming these photocatalytic filters, 70,000 photocatalytic filter materials were bundled.

[0067] Air containing benzene was used as a disposal fluid, and the benzene was detected for concentrations in two places on an air introduction side and air discharge side of the photocatalytic filter, and the benzene removal ratio was calculated on the basis of the expression;

$$\text{Removal ratio} = 1 - \left(\frac{Cd}{Ci} \right)$$

Cd: benzene concentration on air discharge side

Ci: benzene concentration on air introduction side

[0068] The benzene concentration on the air introduction side was varied, and a change in the benzene removal ratio was observed to evaluate each of the photocatalytic filter devices 200 for performances.

[0069] Fig. 10 shows evaluation results, in which a curve "a" shows a change in the benzene removal ratio in Example 1 and a curve "b" shows a change in the benzene removal ratio in Comparative Example 1. When the benzene concentration on the introduction side is increased, the benzene removal ratio attained by the photocatalytic filter in each of Example 1 and Comparative Example 1 decreases. However, the decrease in the removal ratio in Example 1 is small, while the removal ratio in Comparative Example 1 sharply decreases.

[0070] The reason for the above results is as follows. In the photocatalytic filter in Example 1, air can be allowed to flow uniformly like water stream shown in the

water stream test in Fig. 6, so that the photocatalytic filter can maintain its function as a filter and a decrease in the trapped benzene amount can be suppressed. In the photocatalytic filter in Comparative Example 1, air cannot be allowed to flow uniformly like water stream shown in the water stream test in Fig. 13, so that the benzene trapping ratio (adsorption ratio) is decreased and that the removal ratio is decreased.

[0071] When the benzene concentration on the air introduction side is low, a difference between Example 1 and Comparative Example 1 is not so clear as compared with the counterpart when the benzene concentration is high. It is assumed that the concentration on the air discharge side is very low and close to a detection limit of the gas chromatography used, so that a measurement error is caused. It is assumed that the difference only appears to be small and that a larger difference is virtually present between these two.

[0072] As explained in detail hereinabove, according to the light-transmittable linear photocatalytic filter material of the present invention, the height from the outer side surface of the filter material to the photocatalyst layer in the central region thereof is smaller than the counterpart in each end region. When a number of such filter materials are bundled to constitute a filter, therefore, the cross section of each filter material has the outer side form of a Japanese hand drum or tsuzumi (that is, a central region of outer side surface of the filter is inwardly curved) instead of a barrel, and such filter materials can be arranged in the longitudinal direction substantially in parallel with one another. Further, when a disposal fluid is allowed to flow through spaces among the filter materials, the fluid can be allowed to flow substantially uniformly, so that the removal ratio of contaminants in the disposal fluid can be improved.

[0073] According to the process for the production of a light-transmittable linear photocatalytic filter material, provided by the present invention, a number of the above filter materials can be produced simultaneously in a simple step at high yields.

Claims

1. A light-transmittable linear photocatalytic filter material comprising a light-transmittable linear material, a number of particulate materials bonded to an outer side surface of the light-transmittable linear material and a photocatalyst layer formed on said outer side surface and said number of particulate materials, said light-transmittable linear photocatalytic filter material being for the production of a light-transmittable linear photocatalytic filter in which light enters one end or both ends of said light-transmittable linear material, propagates inside said light-transmittable linear material and leaks into said photocatalyst layer and said photocatalyst layer

er is irradiated with the leaked light, characterized in that:

a maximum value of heights from the outer side surface of the linear material to the surface of the photocatalyst layer in a central region of said light-transmittable linear material in the longitudinal direction is smaller than a maximum value of heights from the outer side surface of the linear material to the surface of the photocatalyst layer in regions of both ends thereof.

2. The light-transmittable linear photocatalytic filter material of claim 1, wherein the central region of the outer surface of said light-transmittable linear material in the longitudinal direction has a length in the range of from 20 % to 60 % based on the total length of said outer surface; each end region of the outer surface of said light-transmittable linear material in the longitudinal direction has a length in the range of from 20% to 40% based on said total length; and said particulate materials distributed in said central region has a lower density than said particulate materials distributed in each end region.
3. A light-transmittable linear photocatalytic filter material of any of the preceding claims, wherein the light-transmittable linear material is a fiber-shaped or rod-shaped linear material that transmits light.
4. A light-transmittable linear photocatalytic filter material of any of the preceding claims, wherein the light transmittable linear material has its internal transmittance of at least 90% per 10 cm of a length thereof.
5. A light-transmittable linear photocatalytic filter material of any of the preceding claims, wherein the light transmittable linear material is selected from a quartz glass fiber and multi component glass fiber made of silicon dioxide as a main component.
6. A light-transmittable linear photocatalytic filter material of any of the preceding claims, wherein particulate materials are spherical and have a particle diameter d which is in the range of 4% to 70% based on the diameter D of the linear material.
7. A light transmittable linear photocatalytic filter material of claim 1, wherein particulate materials are made of quartz glass.
8. A light-transmittable linear photocatalytic filter material of claim 1, wherein the photocatalyst layer is made of titanium dioxide.
9. A light-transmittable linear photocatalytic filter com-

prising a bundle of a large number of light-transmittable linear photocatalytic filter materials recited in claim 1.

10. A process for producing light-transmittable linear photocatalytic filter materials each of which is made of a long and narrow linear material, a number of particulate materials, a long and narrow linear material that are bonded to an outer side surface of the linear material in a predetermined distribution density, and a photocatalyst layer formed on said outer surface and said particulate materials, comprising the steps of:

mixing a number of light-transmittable linear materials, a number of particulate materials and a predetermined amount of an adhesive to temporarily bond said light transmittable linear materials and said particulate materials, housing said light-transmittable linear materials and said particulate materials that are temporarily bonded, in a container having a pair of facing net-shaped surfaces, placing weights having a bottom having a predetermined area and having a predetermined loading weight on central portions of said net-shaped surfaces to press said light-transmittable linear materials and said particulate materials, and rocking or vibrating said container in a state where said light-transmittable linear materials and said particulate materials are pressed, for a predetermined time period, to rub off particulate materials on a central region of said temporarily bonded linear materials in the longitudinal direction.

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Fig. 1

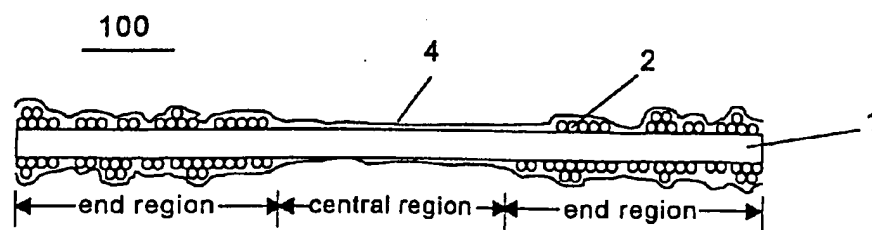


Fig. 2

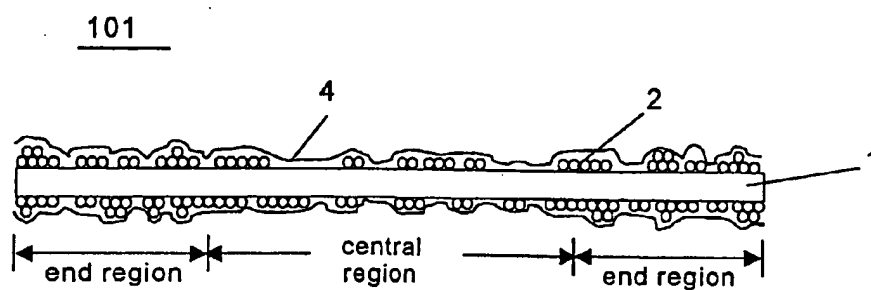


Fig. 3

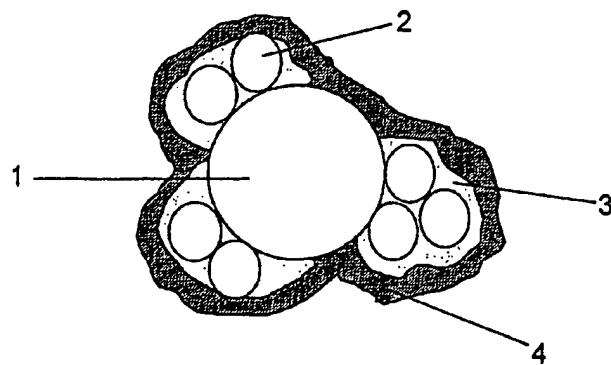


Fig. 4

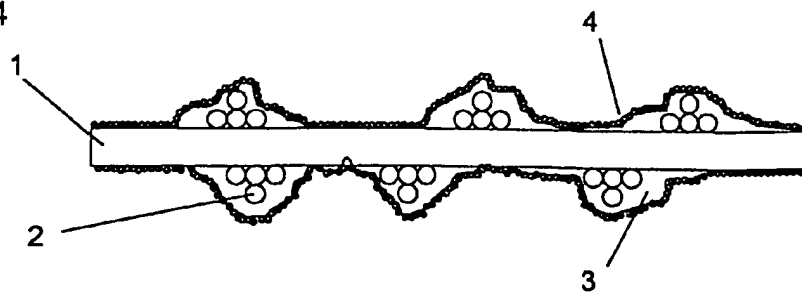


Fig. 5

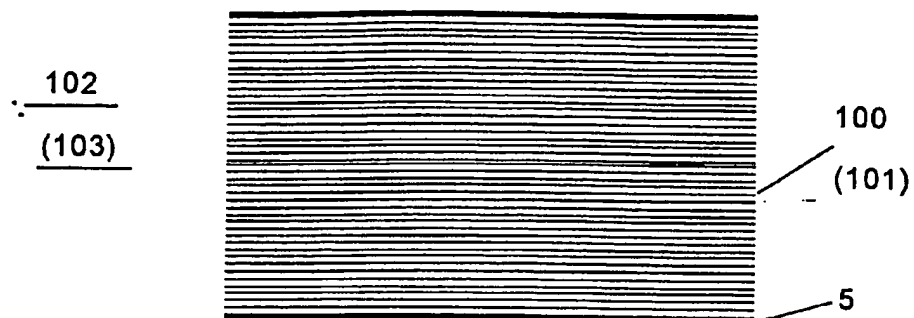


Fig. 6

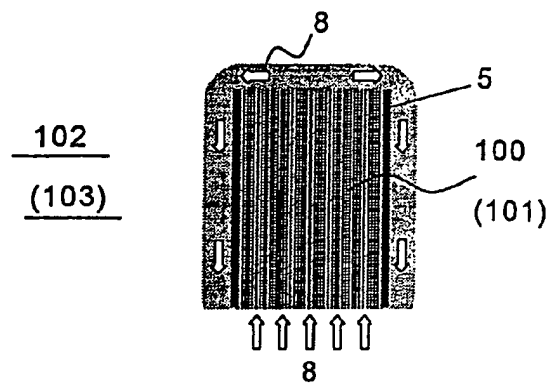


Fig. 7

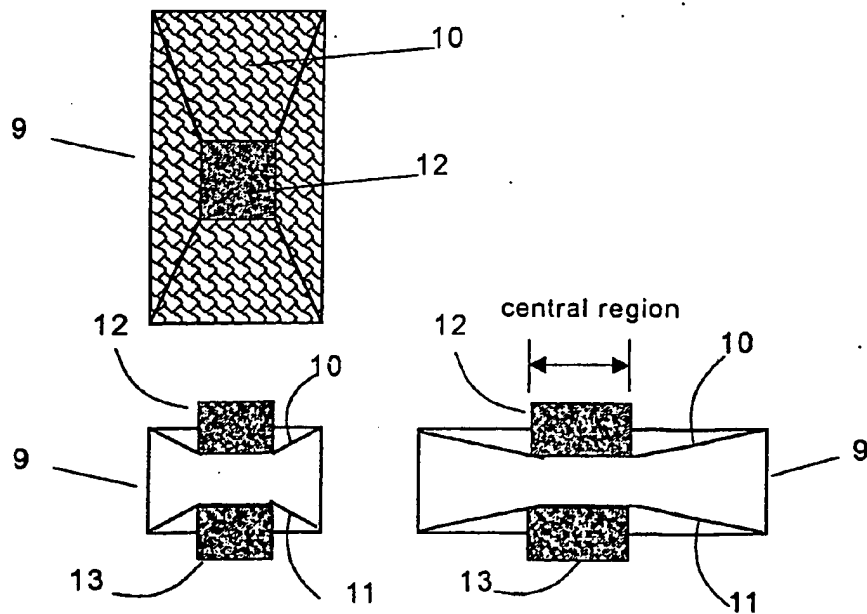


Fig. 8

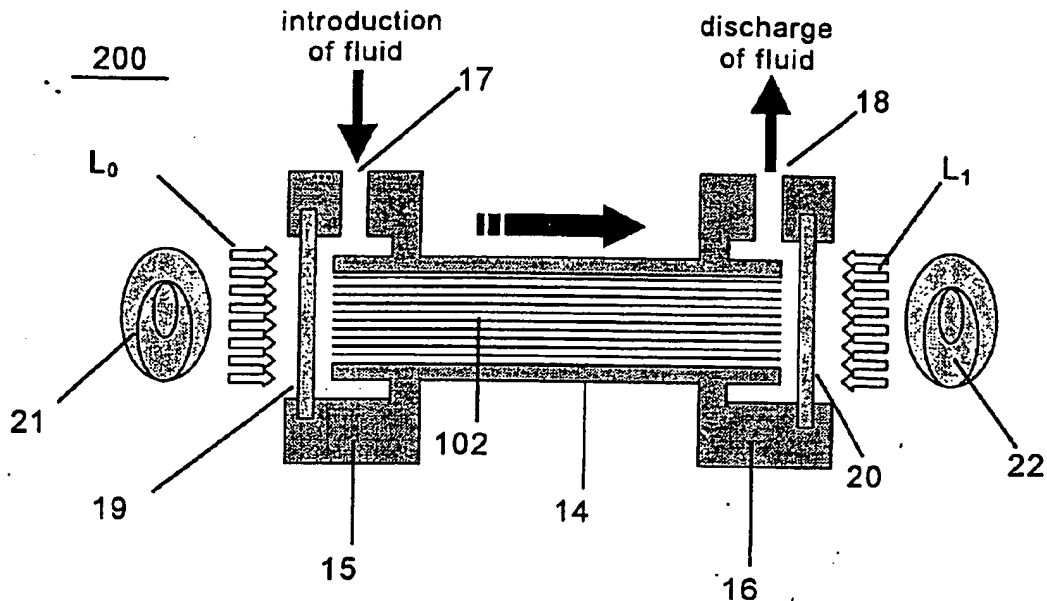


Fig. 9

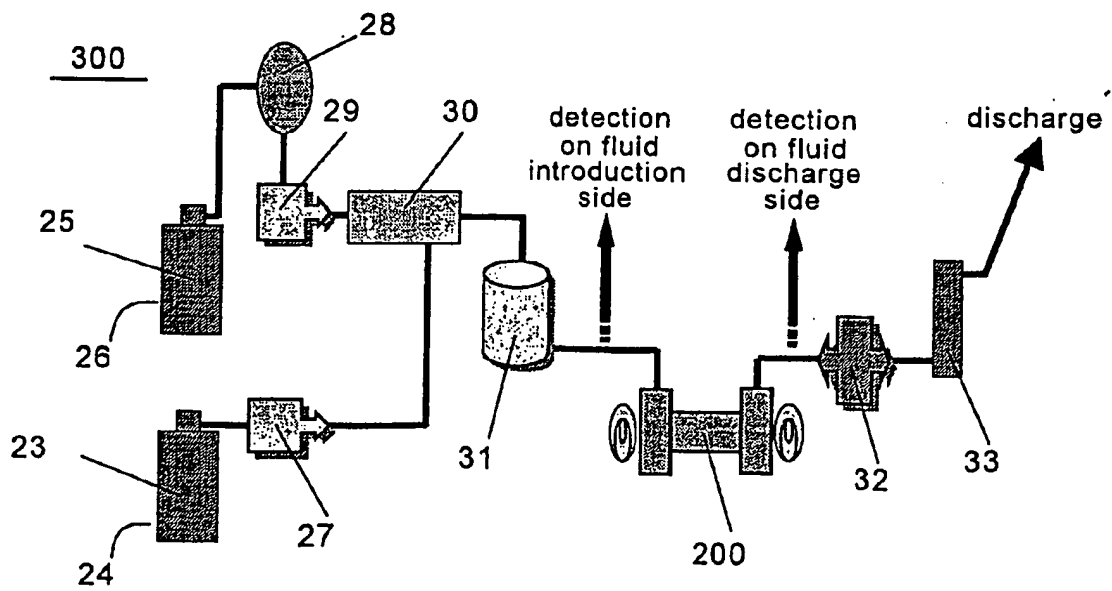


Fig. 10

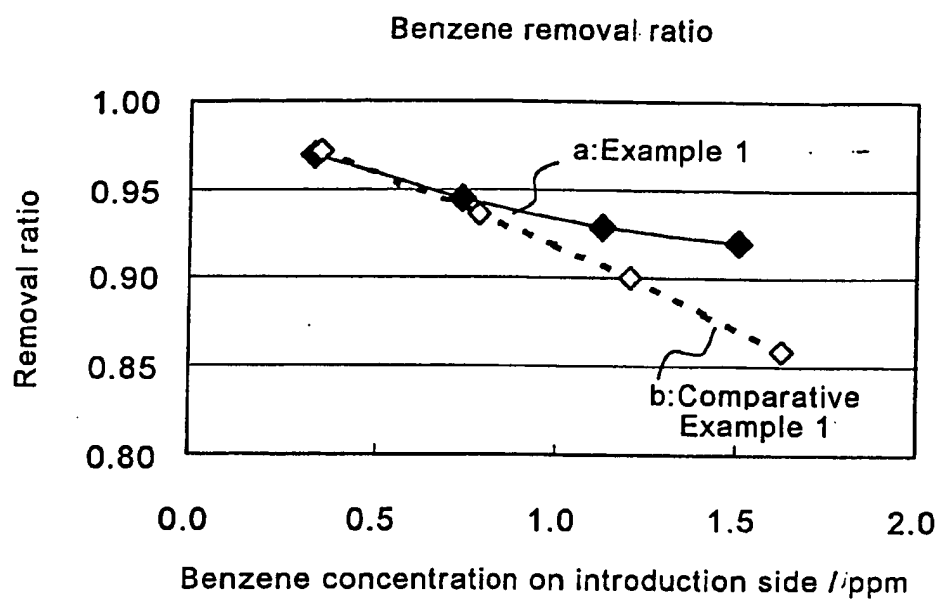


Fig. 11

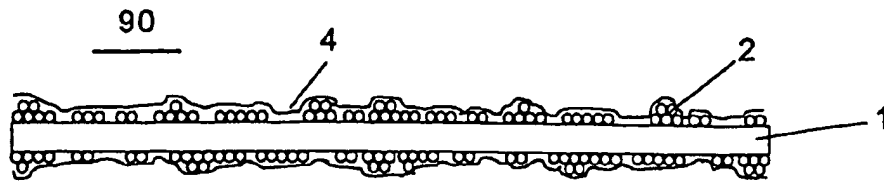


Fig. 12

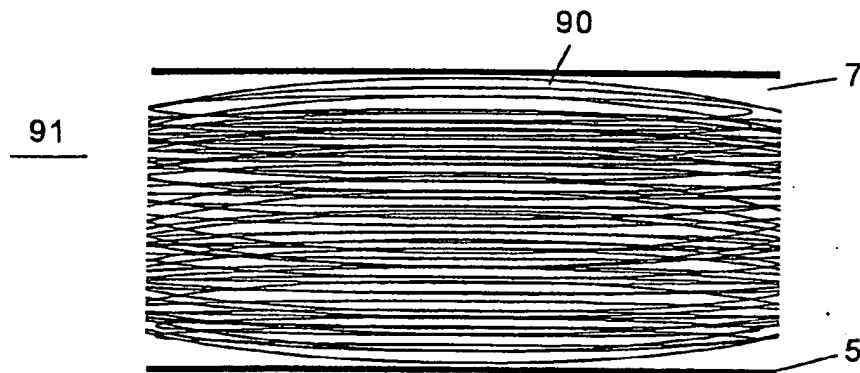
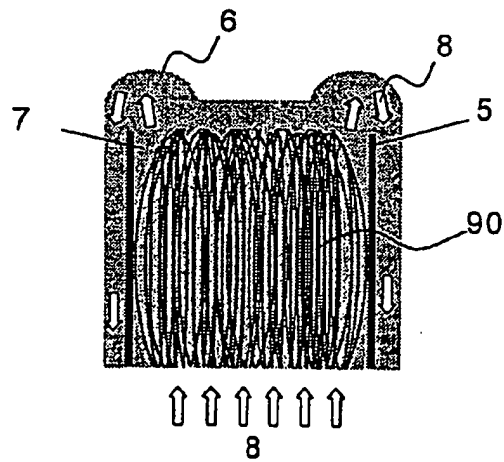


Fig. 13





European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 02 02 1779

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			B01D B01J
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 4 February 2003	Examiner Bertram, H
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document</p> <p>T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons A: member of the same patent family, corresponding document</p>			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 02 1779

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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